Applied Surface Science 332 (2015) 384–392

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Theoretical and experimental investigations on corrosion control of 65Cu–35Zn brass in nitric acid by two thiophenol derivatives

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ARTICLE INFO

Article history:
Received 27 November 2014
Received in revised form 16 January 2015
Accepted 21 January 2015
Available online 31 January 2015

Keywords:
Brass
Inhibitor
Corrosion
Adsorption
Quantum chemical study

ABSTRACT

Inhibitive performance of two thiophenol derivatives namely 4-aminothiophenol (4-ATP) and 4-amino phenol disulfide (4-APD) on corrosion behavior of 65Cu–35Zn brass in 0.5 M HNO_3 was investigated. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) and also quantum chemical study were used. 4-APD showed higher efficiency at low temperatures while for higher temperatures the 4-ATP is more efficient. The inhibitors obey Langmuir isotherm and its adsorption is both chemical and physical type. Quantum chemical study reveals that the benzene ring, S and N atoms can be suitable sites for adsorption onto surface. Finally, an acceptable correlation between the theoretical and experimental inhibitor efficiency was acquired.

1. Introduction

Copper and its alloys are widely used in industry especially in heating and cooling system because of their excellent electrical and thermal conductivity [1]. Brass is broadly used as tubing material for condensers and heat exchangers in various cooling water systems [2–5]. This family of copper alloys is susceptible to a corrosion process known as dezincification and it susceptibly increases as zinc content increases [6]. Among the corrosive media, the nitric acid is recognized as a strong oxidizing agent that is able to corrode copper and its alloys quite easily. In this respect, the corrosion of brass in this environment has been subjected to extensive researches [7–11]. Among methods which have been applied to minimize the dezincification phenomenon, the use of inhibitors is most efficient one. In this way, many types of organic and inorganic chemical compounds have been introduced as the corrosion inhibitor for copper and its alloys [12–29]. The inhibition mechanism is generally explained that inhibitor molecules which are able to donate electrons, form coordinative bonds in the presence of vacant *d*-orbitals in copper [5]. Interaction with rings containing conjugated bonds, π-electrons, is also suggested [30]. Thus, frequently heterocyclic organic compounds which contain nitrogen, sulfur and/or oxygen atoms (having non-bonding electrons) in molecular structure are synthesized [31,32]. Since, they are frequently responsible for good corrosion inhibition due to physically and/or chemically adsorption onto the surface [31,33–35].

Recently, it has been attempted to combine theoretical and practical approaches to investigate compounds with similar structure and find models that would enable to produce newly synthesized compounds acting as corrosion inhibitor. In this way, the quantum chemical methods enable the definition of a large number of molecular quantities characterizing the reactivity, shape, and binding properties of a complete molecule [36]. Highest occupied molecular orbital energy (E_{HOMO}) and lowest unoccupied molecular orbital energy (E_{LUMO}), also called frontier orbitals, determine the way the molecule interacts with other species [37]. Therefore, invaluable parameters acquired by quantum chemical method can help to understand the adsorption properties by considering the structure of every individual molecule.

In this work, corrosion inhibition of two different thiophenol derivatives namely 4-aminothiophenol (4-ATP) and 4-amino phenol disulfide (4-APD) on 65–35 brass alloy in nitric acid (HNO_3) solution has been studied. Electrochemical methods including potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) have been employed to investigate the effect of concentration and temperature on inhibitive behavior of these compounds. Also, quantum chemical method has been used for identification of adsorption type and modeling corrosion inhibition by means of quantum chemical indices. It is also noticeable that there is almost no investigation on the effect of thiophenol derivatives as corrosion inhibitor for brass alloys.

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http://dx.doi.org/10.1016/j.apsusc.2015.01.178
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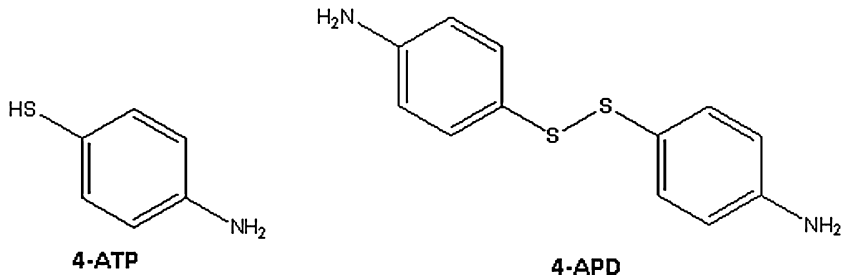

Fig. 1. Molecular structures of (a) 4-aminothiophenol (4-ATP) and (b) 4-amino phenol disulfide (4-APD).

2. Materials and methods

Fig. 1 shows molecular structure of the two thiophenol derivatives, 4-ATP and 4-APD. 4-ATP was Merck product, and 4-APD was synthesized from 4-ATP compound according to the procedure reported previously [33]. The electrolyte solution was 0.5 M HNO_3 and four inhibitor concentrations of 50, 100, 150 and 200 ppm (mg/L) were chosen. The reference and auxiliary electrode were saturated calomel electrode (SCE) and a 2 cm^2 foil of platinum, respectively. Working electrode was a sheet of 65–35 brass alloy and its chemical composition was as follow (wt%): 65% Cu and 35% Zn and other alloying elements were trace. The sample was then cold mounted in a self-cure epoxy resin, resulting in 1.29 cm^2 exposed area. Before each electrochemical measurement, the samples were mechanically ground with emery papers down to 1200 grade, then washed with distilled water and finally dried with air flow. Also, the working electrode was immersed in the prepared solution for 45 min until corrosion potential approached to a steady state condition. The all electrochemical tests were performed by means of ACM instrument (Gill AC) laboratory potentiostat. Potentiodynamic polarization was conducted at a constant sweep rate of 60 mV/min with a scanning range of −250 to +250 mV around the open circuit potential (OCP). All tests were carried out at constant temperature (±1 °C) by controlling the cell temperature using a water bath. EIS measurements were performed in the frequency range of 10 kHz to 10 mHz with amplitude of 15 mV peak-to-peak using AC signals at OCP.

The molecular structures of the both investigated compounds have been geometrically optimized by DFT method using B3LYP level and 3-21G** basis set with Gaussian 98. Quantum chemical parameters such as the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and dipole moment (μ) have been calculated.

3. Results and discussion

3.1. Potentiodynamic polarization

Cathodic and anodic polarization plots of 65Cu–35Zn brass with different concentrations of 4-ATP and 4-APD in 0.5 M HNO_3 at 25 °C have been presented in Fig. 2. Electrochemical parameters including corrosion potential (E_{corr}), corrosion current density (i_{corr}) and cathodic and anodic Tafel slopes (β_c and β_a) have been measured by Tafel extrapolating of the anodic and cathodic lines and listed in Table 1. Also, the surface coverage (θ) and the inhibition efficiency ($\%\eta$) have been calculated using the following equations [38,39]:

$$\theta = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \quad (1)$$

$$\%\eta = \theta \times 100 \quad (2)$$

where i^0_{corr} and i_{corr} are corrosion current densities of brass in absence and presence of inhibitor, respectively. Fig. 2 shows that both inhibitors diminish cathodic and anodic current densities so that the decrease in cathodic branch is more considerable. In addition, it can be seen that significant dissolution of metal at potentials higher than 100 mV with respect to OCP give rise to desorption of the inhibiting layer and consequently an increase in current of anodic branches. By assessing Table 1, it can be observed that the values of corrosion current density in presence of inhibitors (i_{corr}) are significantly lower than the uninhibited solution. Also, a considerable increase in cathodic Tafel slope for the inhibited solutions is obvious. Furthermore, change in the anodic Tafel slope is insignificant. Considering efficiency values, it is clear that the inhibition effectiveness of 4-APD increases with increasing in inhibitor concentration. However, in the case of 4-ATP, there is an optimum inhibitor concentration (i.e. 150 ppm) with highest efficiency so

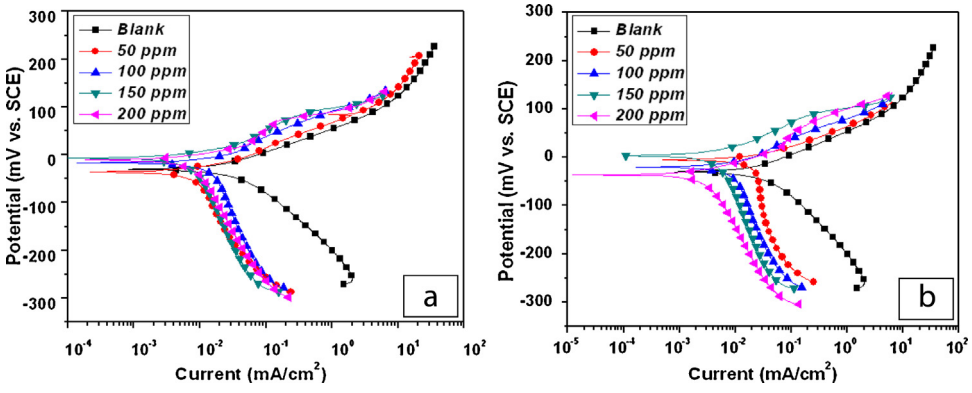

Fig. 2. Effect of concentration of (a) 4-ATP and (b) 4-APD on potentiodynamic polarization curves of 65Cu–35Zn brass in 0.5 M HNO_3 at 25 °C.